Crystal structure of 3,3-bis(*tert*-butyl-cyclopentadienyl)-bicyclo[3.1.0]hex-3-zircona-1(5)-ene-6-nickela-6,6-bis(triphenylphosphine), $(C_9H_{13})_2(ZrC_4H_4)Ni(C_{18}H_{15}P)_2$

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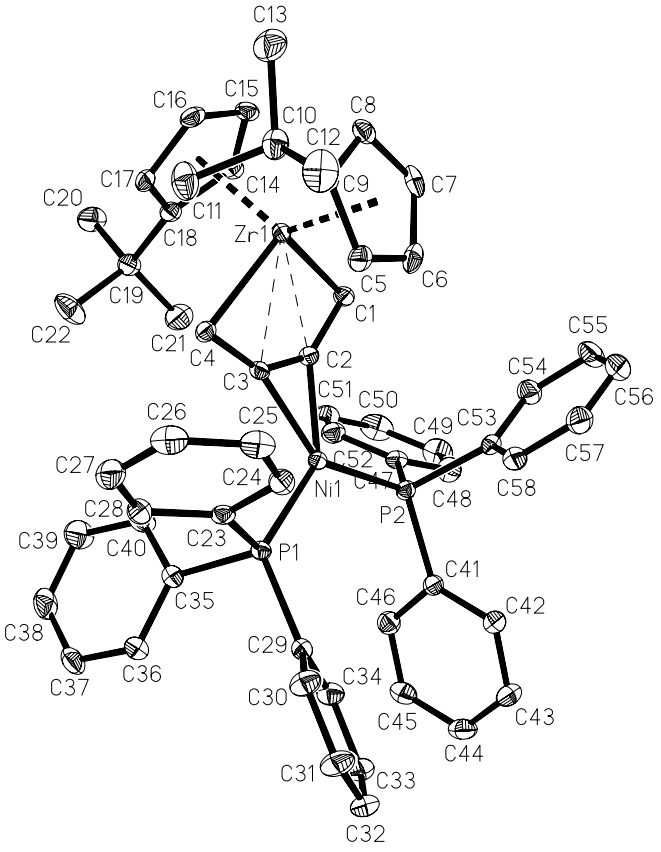

Abstract

$C_{58}H_{60}NiP_2Zr$, monoclinic, $P12_1/n1$ (no. 14), a = 12.378(3) Å, b = 10.353(2) Å, c = 38.031(8) Å, β = 95.74(3)°, V = 4849.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.054, T = 200 K.

Source of material

The complex (*t*-Bu-$C_5H_4)_2Zr(\eta^4$-$H_2C_4H_2)$ (0.38 g, 0.98 mmol) was dissolved in THF (15 ml) and a dark yellow solution of $(C_2H_4)Ni(PPh_3)_2$ (0.6 g, 0.98 mmol) in THF (10 ml) was added. The reaction mixture was stirred at 323 K for 48 hours. After that time all volatiles were removed in vacuum and the remaining yellow powder was washed three times with cold (253 K) *n*-hexane (2 ml). The *n*-hexane containing powder was dried in vacuum and dissolved in hot THF (5 ml). The dark yellow solution was allowed to cool down to room temperature during 24 hours in a dewar, initially filled with hot water, to yield yellow crystals.

Experimental details

The H atoms (except the H atoms attached to C1 and C4) are added geometrically and refined using the riding model.

Discussion

We recently reported that unsubstituted 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4$-$H_2C_4H_2)$ reacts with equimolar amounts of the nickel(0) complexes $L_2Ni(\eta^2$-$C_2H_4)$ (L = PPh_3 or PCy_3) in THF at room temperature to give the binuclear complexes $Cp_2Zr[\mu(\eta^4$-$H_2C_4H_2)]NiL_2$ [1]. Additionally, the complex $Me_2Si(\eta^5$-$C_5H_4)_2Zr[\mu(\eta^4$-$H_2C_4H_2)]Ni(PPh_3)_2$ was investigated [2]. These molecules are not planar with regard to the moiety $ZrC_\alpha C_\beta C_{\beta'} C_{\alpha'}Ni$. In contrast to that the structure of the here presented complex was calculated (B3LYP/LANL2DZ) to be planar due to the sterical influence of the *tert*-butyl groups [3]. To prove the DFT predictions we performed the X-ray crystal structure analysis of the title compound which shows a high steric demand. The molecular structure of (*t*-Bu-$C_5H_4)_2Zr[\mu(\eta^4$-$C_4H_4)]Ni(PPh_3)_2$ is almost similar to that of the unsubstituted compound. The complex displays beside a bent zirconocene an additional butyne-1,4-diyl ligand, which coordinates with its triple bond a Ni(0) center. The bonding distance C2—C3 is 1.308(2) Å and in the range of a double bond. The coordination environment at the Ni(0) center is slightly distorted trigonal planar. The angle between the planes defined by Ni1, C2, C3 and Ni1, P1, P2 is 4.9°. The part of the molecule $ZrC_\alpha C_\beta C_{\beta'} C_{\alpha'}Ni$ is not planar. Angles between the planes defined by $ZrC_\alpha C_{\alpha'}$ and $C_\alpha C_\beta C_{\beta'} C_{\alpha'}$ of 15.6° and between the latter plane and $C_\beta C_{\beta'}Ni$ of 13.2° were obtained. The deviation from the calculated data may be due to packing effects.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.25 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.06 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	49.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	55594, 8125
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6710
$N(param)_{refined}$:	575
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(5)	4*e*	0.7690	1.1985	0.1186	0.036
H(6)	4*e*	0.9554	1.2207	0.0989	0.041
H(7)	4*e*	0.9351	1.2632	0.0332	0.041
H(8)	4*e*	0.7355	1.2719	0.0130	0.035
H(11A)	4*e*	0.4508	1.1435	0.0770	0.069
H(11B)	4*e*	0.5599	1.0968	0.0995	0.069
H(11C)	4*e*	0.5393	1.0625	0.0584	0.069
H(12A)	4*e*	0.4903	1.3673	0.0976	0.076
H(12B)	4*e*	0.6019	1.4359	0.0905	0.076
H(12C)	4*e*	0.6018	1.3227	0.1191	0.076
H(13A)	4*e*	0.4537	1.3155	0.0334	0.073
H(13B)	4*e*	0.5434	1.2428	0.0133	0.073
H(13C)	4*e*	0.5642	1.3877	0.0269	0.073
H(14)	4*e*	0.9110	0.8801	–0.0083	0.032
H(15)	4*e*	0.7926	1.0721	–0.0252	0.034
H(16)	4*e*	0.6149	1.0416	0.0011	0.035
H(17)	4*e*	0.6243	0.8316	0.0345	0.032
H(20A)	4*e*	0.8195	0.5001	–0.0020	0.065
H(20B)	4*e*	0.8461	0.6264	–0.0238	0.065
H(20C)	4*e*	0.7234	0.5949	–0.0168	0.065
H(21A)	4*e*	0.9443	0.7034	0.0650	0.072
H(21B)	4*e*	0.9800	0.6885	0.0259	0.072
H(21C)	4*e*	0.9491	0.5633	0.0475	0.072
H(22A)	4*e*	0.7500	0.6577	0.0758	0.078
H(22B)	4*e*	0.7633	0.5189	0.0582	0.078
H(22C)	4*e*	0.6660	0.6120	0.0435	0.078
H(24)	4*e*	0.8285	1.1079	0.1891	0.036
H(25)	4*e*	0.6586	1.2063	0.1853	0.044
H(26)	4*e*	0.5020	1.0804	0.1824	0.049
H(27)	4*e*	0.5160	0.8563	0.1847	0.049
H(28)	4*e*	0.6862	0.7572	0.1901	0.038
H(30)	4*e*	0.8364	0.9772	0.2542	0.043
H(31)	4*e*	0.9091	1.0018	0.3128	0.050
H(32)	4*e*	1.0803	0.9220	0.3314	0.047
H(33)	4*e*	1.1807	0.8182	0.2914	0.044
H(34)	4*e*	1.1101	0.7935	0.2326	0.038
H(36)	4*e*	0.8886	0.6411	0.2414	0.038
H(37)	4*e*	0.8618	0.4192	0.2352	0.048
H(38)	4*e*	0.8409	0.3259	0.1796	0.053
H(39)	4*e*	0.8497	0.4527	0.1295	0.061
H(40)	4*e*	0.8833	0.6736	0.1355	0.048
H(42)	4*e*	1.2745	1.0811	0.2084	0.038
H(43)	4*e*	1.3821	1.0202	0.2595	0.046
H(44)	4*e*	1.4275	0.8046	0.2696	0.048
H(45)	4*e*	1.3621	0.6474	0.2291	0.044
H(46)	4*e*	1.2548	0.7066	0.1779	0.039
H(48)	4*e*	1.3862	0.9373	0.1281	0.044
H(49)	4*e*	1.4817	0.8155	0.0903	0.058
H(50)	4*e*	1.3944	0.6519	0.0561	0.061
H(51)	4*e*	1.2104	0.6144	0.0587	0.053
H(52)	4*e*	1.1129	0.7385	0.0959	0.039
H(54)	4*e*	1.2677	1.0998	0.0960	0.043
H(55)	4*e*	1.2715	1.3222	0.0857	0.056
H(56)	4*e*	1.1883	1.4643	0.1220	0.057
H(57)	4*e*	1.0984	1.3854	0.1682	0.049
H(58)	4*e*	1.0928	1.1645	0.1786	0.038
H(1A)	4*e*	1.053(2)	1.043(2)	0.0662(5)	0.023(5)
H(1B)	4*e*	1.021(2)	0.908(2)	0.0462(5)	0.036(5)
H(4A)	4*e*	0.713(2)	0.964(2)	0.1201(5)	0.031(5)
H(4B)	4*e*	0.712(2)	0.843(2)	0.0950(5)	0.037(6)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.9978(1)	0.9772(2)	0.06195(4)	0.0242(9)	0.030(1)	0.0194(8)	–0.0032(8)	0.0046(7)	0.0026(8)
C(2)	4*e*	0.9557(1)	0.9334(2)	0.09418(4)	0.0238(9)	0.0224(9)	0.0203(8)	–0.0006(7)	–0.0002(7)	0.0001(7)
C(3)	4*e*	0.8659(1)	0.9139(2)	0.10880(4)	0.0274(9)	0.0214(9)	0.0163(8)	–0.0030(7)	0.0030(7)	0.0019(7)
C(4)	4*e*	0.7482(1)	0.9226(2)	0.10162(4)	0.0212(9)	0.030(1)	0.0190(8)	–0.0046(8)	0.0019(7)	–0.0008(7)
C(5)	4*e*	0.7849(2)	1.2164(2)	0.09513(5)	0.039(1)	0.022(1)	0.0273(9)	–0.0007(8)	–0.0008(8)	–0.0083(7)
C(6)	4*e*	0.8889(2)	1.2279(2)	0.08419(5)	0.030(1)	0.023(1)	0.048(1)	–0.0041(8)	–0.0050(8)	–0.0106(9)
C(7)	4*e*	0.8777(2)	1.2521(2)	0.04772(5)	0.033(1)	0.0180(9)	0.053(1)	–0.0055(8)	0.0146(9)	0.0020(8)
C(8)	4*e*	0.7662(2)	1.2569(2)	0.03655(5)	0.039(1)	0.0183(9)	0.0299(9)	–0.0012(8)	0.0047(8)	0.0022(7)
C(9)	4*e*	0.7069(1)	1.2358(2)	0.06573(5)	0.0293(9)	0.0170(9)	0.0311(9)	–0.0024(7)	0.0025(7)	–0.0030(7)
C(10)	4*e*	0.5847(2)	1.2532(2)	0.06731(5)	0.028(1)	0.031(1)	0.043(1)	0.0005(8)	0.0043(8)	–0.0035(9)
C(11)	4*e*	0.5286(2)	1.1278(2)	0.07635(7)	0.030(1)	0.041(1)	0.068(2)	–0.0051(9)	0.014(1)	0.001(1)
C(12)	4*e*	0.5682(2)	1.3540(2)	0.09628(6)	0.042(1)	0.047(1)	0.065(2)	0.006(1)	0.017(1)	–0.013(1)
C(13)	4*e*	0.5318(2)	1.3044(2)	0.03208(6)	0.034(1)	0.048(1)	0.062(1)	0.006(1)	–0.007(1)	0.002(1)
C(14)	4*e*	0.8396(2)	0.8934(2)	–0.00187(4)	0.037(1)	0.028(1)	0.0159(8)	–0.0014(8)	0.0032(7)	–0.0031(7)
C(15)	4*e*	0.7738(2)	1.0008(2)	–0.01136(4)	0.043(1)	0.026(1)	0.0161(8)	–0.0018(8)	–0.0004(7)	0.0016(7)
C(16)	4*e*	0.6748(2)	0.9838(2)	0.00336(4)	0.034(1)	0.030(1)	0.0221(8)	0.0017(8)	–0.0075(7)	–0.0041(8)
C(17)	4*e*	0.6802(2)	0.8663(2)	0.02189(4)	0.0304(9)	0.029(1)	0.0202(8)	–0.0097(8)	–0.0020(7)	–0.0038(7)
C(18)	4*e*	0.7824(2)	0.8080(2)	0.01881(4)	0.036(1)	0.0234(9)	0.0174(8)	–0.0030(8)	–0.0012(7)	–0.0032(7)
C(19)	4*e*	0.8143(2)	0.6682(2)	0.02764(5)	0.045(1)	0.024(1)	0.0236(9)	–0.0028(8)	0.0002(8)	–0.0037(8)
C(20)	4*e*	0.7995(2)	0.5904(2)	–0.00687(5)	0.065(2)	0.030(1)	0.033(1)	0.004(1)	–0.004(1)	–0.0085(9)
C(21)	4*e*	0.9325(2)	0.6546(2)	0.04287(6)	0.058(1)	0.027(1)	0.057(1)	0.007(1)	–0.015(1)	–0.001(1)
C(22)	4*e*	0.7419(2)	0.6089(2)	0.05361(6)	0.087(2)	0.024(1)	0.048(1)	–0.003(1)	0.021(1)	0.0036(9)
C(23)	4*e*	0.7750(1)	0.9220(2)	0.19003(4)	0.0267(9)	0.029(1)	0.0138(8)	0.0000(8)	0.0036(6)	0.0001(7)
C(24)	4*e*	0.7650(2)	1.0560(2)	0.18844(5)	0.033(1)	0.029(1)	0.0286(9)	–0.0006(8)	0.0043(8)	–0.0006(8)
C(25)	4*e*	0.6640(2)	1.1148(2)	0.18593(5)	0.043(1)	0.036(1)	0.031(1)	0.0129(9)	0.0068(8)	0.0000(8)
C(26)	4*e*	0.5714(2)	1.0404(2)	0.18441(5)	0.033(1)	0.056(2)	0.033(1)	0.014(1)	0.0076(8)	0.003(1)
C(27)	4*e*	0.5798(2)	0.9077(2)	0.18581(5)	0.026(1)	0.059(2)	0.038(1)	–0.004(1)	0.0034(8)	0.005(1)
C(28)	4*e*	0.6813(1)	0.8487(2)	0.18884(5)	0.030(1)	0.037(1)	0.0281(9)	–0.0045(8)	0.0056(8)	0.0026(8)
C(29)	4*e*	0.9650(1)	0.8817(2)	0.23715(4)	0.0270(9)	0.0241(9)	0.0224(8)	–0.0042(7)	0.0038(7)	0.0009(7)
C(30)	4*e*	0.9067(2)	0.9442(2)	0.26153(5)	0.033(1)	0.046(1)	0.027(1)	0.0043(9)	0.0016(8)	–0.0050(9)
C(31)	4*e*	0.9500(2)	0.9589(2)	0.29647(5)	0.048(1)	0.055(1)	0.0227(9)	0.003(1)	0.0036(8)	–0.0096(9)
C(32)	4*e*	1.0512(2)	0.9121(2)	0.30749(5)	0.047(1)	0.048(1)	0.0222(9)	–0.008(1)	–0.0049(8)	0.0012(9)
C(33)	4*e*	1.1104(2)	0.8506(2)	0.28377(5)	0.035(1)	0.043(1)	0.031(1)	–0.0015(9)	–0.0061(8)	0.0068(9)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(34)	4*e*	1.0682(2)	0.8356(2)	0.24877(5)	0.032(1)	0.038(1)	0.0255(9)	0.0032(9)	0.0042(7)	0.0015(8)
C(35)	4*e*	0.8890(1)	0.6807(2)	0.18908(4)	0.0254(9)	0.0228(9)	0.0262(9)	–0.0003(7)	0.0039(7)	0.0017(7)
C(36)	4*e*	0.8819(2)	0.6034(2)	0.21855(5)	0.035(1)	0.033(1)	0.029(1)	–0.0028(8)	0.0041(8)	0.0055(8)
C(37)	4*e*	0.8651(2)	0.4716(2)	0.21481(6)	0.036(1)	0.033(1)	0.051(1)	–0.0034(9)	0.0038(9)	0.019(1)
C(38)	4*e*	0.8531(2)	0.4162(2)	0.18194(6)	0.048(1)	0.022(1)	0.063(2)	–0.0042(9)	0.001(1)	0.004(1)
C(39)	4*e*	0.8588(2)	0.4909(2)	0.15231(6)	0.082(2)	0.027(1)	0.043(1)	–0.005(1)	0.001(1)	–0.0065(9)
C(40)	4*e*	0.8778(2)	0.6224(2)	0.15593(5)	0.068(2)	0.024(1)	0.029(1)	–0.005(1)	0.0044(9)	0.0003(8)
C(41)	4*e*	1.2535(1)	0.9005(2)	0.18754(4)	0.0218(9)	0.030(1)	0.0227(8)	–0.0031(8)	0.0039(7)	0.0005(7)
C(42)	4*e*	1.2922(2)	0.9926(2)	0.21232(5)	0.033(1)	0.030(1)	0.030(1)	–0.0021(8)	–0.0011(8)	0.0003(8)
C(43)	4*e*	1.3563(2)	0.9564(2)	0.24276(5)	0.040(1)	0.047(1)	0.028(1)	–0.007(1)	–0.0049(8)	–0.0032(9)
C(44)	4*e*	1.3829(2)	0.8287(2)	0.24885(5)	0.035(1)	0.055(1)	0.029(1)	0.002(1)	–0.0009(8)	0.010(1)
C(45)	4*e*	1.3446(2)	0.7358(2)	0.22480(5)	0.038(1)	0.038(1)	0.036(1)	0.0059(9)	0.0056(8)	0.0097(9)
C(46)	4*e*	1.2807(2)	0.7712(2)	0.19442(5)	0.034(1)	0.032(1)	0.032(1)	–0.0009(8)	0.0043(8)	–0.0001(8)
C(47)	4*e*	1.2390(1)	0.8508(2)	0.11570(4)	0.0295(9)	0.028(1)	0.0202(8)	0.0021(8)	0.0023(7)	0.0017(7)
C(48)	4*e*	1.3498(2)	0.8721(2)	0.11389(5)	0.033(1)	0.041(1)	0.037(1)	–0.0006(9)	0.0085(8)	–0.0035(9)
C(49)	4*e*	1.4067(2)	0.7993(2)	0.09164(6)	0.039(1)	0.058(2)	0.050(1)	0.010(1)	0.019(1)	0.002(1)
C(50)	4*e*	1.3548(2)	0.7026(2)	0.07115(6)	0.064(2)	0.051(1)	0.041(1)	0.021(1)	0.022(1)	–0.002(1)
C(51)	4*e*	1.2461(2)	0.6804(2)	0.07276(5)	0.063(2)	0.036(1)	0.032(1)	0.008(1)	0.003(1)	–0.0079(9)
C(52)	4*e*	1.1881(2)	0.7544(2)	0.09497(5)	0.038(1)	0.031(1)	0.0270(9)	0.0022(9)	0.0008(8)	–0.0008(8)
C(53)	4*e*	1.1817(1)	1.1087(2)	0.13899(4)	0.0223(9)	0.029(1)	0.0234(8)	–0.0043(7)	–0.0020(7)	0.0009(7)
C(54)	4*e*	1.2336(2)	1.1572(2)	0.11095(5)	0.034(1)	0.039(1)	0.035(1)	–0.0042(9)	0.0062(8)	0.0056(9)
C(55)	4*e*	1.2356(2)	1.2896(2)	0.10482(6)	0.048(1)	0.045(1)	0.047(1)	–0.011(1)	0.006(1)	0.019(1)
C(56)	4*e*	1.1859(2)	1.3740(2)	0.12622(6)	0.056(1)	0.031(1)	0.052(1)	–0.006(1)	–0.010(1)	0.011(1)
C(57)	4*e*	1.1331(2)	1.3275(2)	0.15357(5)	0.050(1)	0.029(1)	0.041(1)	0.002(1)	–0.0047(9)	–0.0032(9)
C(58)	4*e*	1.1304(2)	1.1961(2)	0.15981(5)	0.037(1)	0.031(1)	0.0266(9)	–0.0024(8)	0.0015(8)	–0.0005(8)
Ni(1)	4*e*	0.98895(2)	0.90941(2)	0.143986(5)	0.0208(1)	0.0228(1)	0.0168(1)	–0.00277(9)	0.00240(8)	0.00078(9)
P(1)	4*e*	0.91224(3)	0.85534(4)	0.19056(1)	0.0237(2)	0.0217(2)	0.0171(2)	–0.0018(2)	0.0032(2)	0.0002(2)
P(2)	4*e*	1.16207(3)	0.93617(4)	0.14750(1)	0.0221(2)	0.0255(2)	0.0196(2)	–0.0028(2)	0.0025(2)	–0.0017(2)
Zr(1)	4*e*	0.81440(1)	1.02635(2)	0.054350(4)	0.02285(9)	0.01891(9)	0.01703(8)	–0.00294(7)	0.00150(6)	–0.00008(6)

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